

Resonating Valence Bond Quantum Monte Carlo: Application to the ozone molecule

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We study the potential energy surface of the ozone molecule by means of Quantum Monte Carlo simulations based on the resonating valence bond concept. The trial wave function consists of an antisymmetrized geminal power arranged in a single-determinant that is multiplied by a Jastrow correlation factor. Whereas the determinantal part incorporates static correlation effects, the augmented real-space correlation factor accounts for the dynamics electron correlation. The accuracy of this approach is demonstrated by computing the potential energy surface for the ozone molecule in three vibrational states: symmetric, asymmetric and scissoring. We find that the employed wave function provides a detailed description of rather strongly-correlated multi-reference systems, which is in quantitative agreement with experiment.

I. INTRODUCTION

Beside its environmental and chemical importance, ozone plays a significant role in assessing the accuracy of electronic structure methods due to its multi-reference character. The latter is due to static electron correlation that arises in situations with degeneracy or near-degeneracy, as in transition metal chemistry and strongly-correlated systems in general¹. As a consequence, determining the electronic structure of ozone requires an accurate treatment of both, dynamic as well as static electron correlation effects. Hence, computing the total energy, equilibrium geometry and vibrational frequencies of the ozone molecule is a rigorous test for even the most accurate quantum-chemical approaches, such as quantum Monte Carlo (QMC)^{3,4,42}, configuration interaction⁵⁻⁹, coupled-cluster¹⁰⁻²², as well as multi-reference-based methods²³⁻³⁵, just to name a few.

In this work, we study the potential energy surface (PES) of a single O_3 molecule using the resonating valence bond (RVB) theory of the chemical bond, which was first introduced by Pauling in the early days of quantum mechanics^{36,37}. According to the RVB theory, a spin singlet can be formed between any two valence electrons belonging to neighboring atoms. Within this approach, the ground state wave function of a molecule can lower the variational energy by imposing an auxiliary resonating degree of freedom between all valence bond configurations. However, the number of bonds increases exponentially with the number of atoms. Nevertheless, it was realized that a single-determinant wave function combined with a suitable real space correlation term, known as that Jastrow correlation factor³⁸, can be employed to represent a complex RVB state^{39,40}. To that extend, the

variational energy is computed by means of conventional QMC techniques⁴¹⁻⁴³, such as variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC)^{44,45}. The RVB wave function is expanded in terms of molecular orbitals (MOs) and optimized by a constrained energy minimization at constant number of MOs⁴⁶⁻⁴⁸. In this way, an accurate RVB wave function based on a single-determinant is obtained, which allows to study systems with sizable static and dynamic electron correlation^{49,50}.

II. RESONATING VALENCE BOND QUANTUM MONTE CARLO

The RVB wave function, which is referred to as Jastrow antisymmetrized geminal power (J-AGP), is given by a product of a Jastrow correlation factor J and a determinantal part Φ_N , i.e. $\Psi_{J-AGP} = J\Phi_N$ ^{51,52}. Each geminal is described by a symmetric pairing-function $\phi(\mathbf{r}_i, \mathbf{r}_j) = \phi(\mathbf{r}_j, \mathbf{r}_i)$. For an N -electron system, consisting of N^\uparrow spin-up and N^\downarrow spin-down electrons and assuming that $N^\downarrow \leq N^\uparrow$, we can define a pure spin state with a total spin $S = |N^\uparrow - N^\downarrow|/2$ and maximum spin projection $S = S_z^{tot}$ in terms of an antisymmetrized product of N^\downarrow singlet pairs and $2S$ unpaired orbitals $\phi_j(\mathbf{r}_j^\uparrow)$ of the remaining spin-up electrons. The resulting antisymmetrized geminal power (AGP) wave function⁵³, which can be arranged in a single-determinant^{39,40}, reads as

$$\Phi_N(\mathbf{R}) = \mathcal{A} \prod_{i=1}^{N^\downarrow} \phi(\mathbf{r}_i^\uparrow, \mathbf{r}_i^\downarrow) \prod_{j=N^\downarrow+1}^{N^\uparrow} \phi_j(\mathbf{r}_j^\uparrow), \quad (1)$$

where $\mathbf{R} = \{\mathbf{r}_1^\uparrow, \dots, \mathbf{r}_{N^\uparrow}^\uparrow, \mathbf{r}_1^\downarrow, \dots, \mathbf{r}_{N^\downarrow}^\downarrow\}$ indicates the $3N$ dimensional vector of all electron coordinates, while \mathcal{A} is the antisymmetrization operator. In general, breaking number-symmetry leads to the Bardeen-Cooper-Schrieffer (BCS) wave function⁵⁴, whereas breaking spin-symmetry yields unrestricted Hartree-Fock determinants⁵⁵. This is to say that the RVB state corresponds to the Gutzwiller-projected BCS state, while the AGP is the particle-conserving version of the BCS wave function, which accounts for the static electron correlation.

Dynamic correlation effects between the electrons is taken into account by the Jastrow correlation factor

$$J(\mathbf{R}) = \exp \left(\sum_{i < j} f(\mathbf{r}_i, \mathbf{r}_j) \right), \quad (2)$$

where $f(\mathbf{r}_i, \mathbf{r}_j)$ is a two-electron coordinate function just as the previously introduced pairing-function $\phi(\mathbf{r}_i, \mathbf{r}_j)$ and is chosen such as to satisfy the Kato cusp conditions⁵⁶.

Just like any other function of two coordinates, $f(\mathbf{r}_i, \mathbf{r}_j)$ as well as $\phi(\mathbf{r}_i, \mathbf{r}_j)$ can be expressed in terms of single-particle orbitals:

$$\phi(\mathbf{r}_i, \mathbf{r}_j) = \sum_{a,b}^M \sum_{\mu,\nu}^m \lambda_{\mu,\nu}^{a,b} \varphi_\mu^a(\mathbf{r}_i) \varphi_\nu^b(\mathbf{r}_j), \quad (3)$$

where $\varphi(\mathbf{r})$ is an atomic orbital (AO), while m is the number of AOs per atom and M the number of atoms. The coefficients $\lambda_{\mu,\nu}^{a,b}$ are arranged in a quadratic $mM \times mM$ matrix denoted as $\mathbf{\Lambda}$. Moreover, to conserve the total spin, $\mathbf{\Lambda}$ is also symmetric. Assuming that the AOs are non-orthogonal, i.e. $S_{\mu,\nu}^{a,b} = \langle \varphi | \varphi \rangle \neq \mathbf{I}$, diagonalizing $\mathbf{\Lambda}$ corresponds to solving the equation

$$\mathbf{\Lambda} \mathbf{S} \mathbf{P} = \mathbf{P} \mathbf{\Lambda}', \quad (4)$$

where the matrix \mathbf{P} contains the eigenvectors of $\mathbf{\Lambda}$ and diagonal matrix $\mathbf{\Lambda}'$ the associated eigenvalues $|\lambda'_1| \geq |\lambda'_2| \geq \dots |\lambda'_{mM}| \geq 0$. The number of nonzero eigenvalues is equivalent to the rank of $\mathbf{\Lambda}$. Using the identity $\mathbf{P}^T \mathbf{S} \mathbf{P} = \mathbf{I}$ that is identical to $\mathbf{P}^T = (\mathbf{S} \mathbf{P})^{-1}$ and multiplying it to the right of Eq. (4), $\mathbf{\Lambda} = \mathbf{P} \mathbf{\Lambda}' \mathbf{P}^T$ is obtained. From this it follows that Eq. (3) is equivalent to

$$\phi(\mathbf{r}_i, \mathbf{r}_j) = \sum_{k=1}^{n-2S} \lambda'_k \phi_k(\mathbf{r}_i) \phi_k(\mathbf{r}_j) \quad (5)$$

where n is the number of MOs $\phi_k(\mathbf{r}_i)$ that can be written as a linear combination of AOs:

$$\phi_k(\mathbf{r}_i) = \sum_l c_{kl} \varphi_l(\mathbf{r}_i), \quad (6)$$

where c_{kl} are the AO coefficients that independently on the particular basis set used are implicitly dependent on \mathbf{r}_i .

The smallest number of orbitals, which is compatible with an unpolarized N -electron system, is $n = N^\uparrow$. In that case the rank of $\mathbf{\Lambda}$ is also minimal and identical to n and the antisymmetrization operator \mathcal{A} singles out just one Slater determinant (SD). Due to the fact that the determinantal part of the resulting wave function is equivalent to the one of unrestricted Hartree-Fock (HF) theory, we will refer to it as JHF to emphasize the presence of the Jastrow correlation factor. If the orbitals of the SD are determined by means of density functional theory (DFT), the eventual wave function is denoted as JDFT⁵⁷. However, the great appeal of the AGP wave function is that if the rank of $\mathbf{\Lambda}$ is larger than N^\uparrow , it corresponds to a multireference wave function that is able to describe static electron correlation effects, although at the computational cost of a genuine single-determinant approach. We will name the resulting wave function as JAGP. As such, the RVB wave function can be thought of as the natural extension of the HF theory, where the Jastrow correlation factor accounts for the dynamic electron correlation, while for $n > N^\uparrow$ most of the static correlation is recovered.

III. COMPUTATIONAL DETAILS

All of our QMC calculations were performed using the *TurboRVB* program package of Sorella and coworkers⁵⁸. We have employed the two different trial wave functions, the JDFT and the JAGP wave function. In both cases the single-determinant is made of MOs as obtained by DFT within local-density approximation (LDA), as described in Ref. 57. In case of the JAGP wave function all parameters were variationally optimized at the VMC level of theory using the stochastic reconfiguration algorithm⁵⁹⁻⁶¹, while for the JDFT wave function the parameters of the Jastrow factor were held fixed. Scalar-relativistic energy consistent pseudopotentials⁶² were used to describe two core electrons of the oxygen atoms. For the single-determinant we employed an atomic basis set consisting of contracted $10s, 8p, 6d, 4f$ Gaussian-type orbitals, while for the Jastrow correlation factor uncontracted $2s, 2p, 1d$ Gaussian-type orbitals were used. The variational energies were computed using two different QMC methods, VMC and the even more accurate lattice-regularised diffusion Monte Carlo (LRDMC) projection technique⁶³, which eventually results in four trial wave functions we have investigated here: JDFT-VMC, JDFT-LRDMC, JAGP-VMC and JAGP-LRDMC.

IV. RESULTS AND DISCUSSION

The PES of the O_3 molecule exhibits two types of minima, one of C_{2v} symmetry (open minimum) with an apex angle of 116.75° and another one of D_{3h} symmetry (ring minimum), where the oxygen atoms form an equilateral

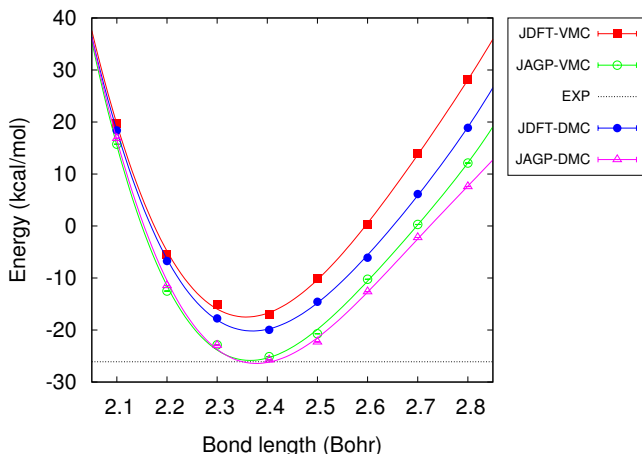


FIG. 1. (colour online) The PES of the $O_3(\tilde{X})$ molecule in a symmetrical vibration state as obtained by the JDFT-VMC, JDFT-LRDMC, JAGP-VMC and JAGP-LRDMC methods. The energy normalization is such that zero energy corresponds to the ground state energy of $O_2(^3\Sigma_g^-) + O(^3P)$. The experimental dissociation energy is illustrated by the dotted line.

triangle. Due to the fact that the open structure is energetically significantly lower than the closed ring case, we will confine ourselves to the O_3 molecule with C_{2v} symmetry only. Symmetry considerations suggest the existence of three open minima, which are separated by energetically high barriers and thus can be considered as independent from each other⁶⁴. As a consequence, the potential energy $E(d_1, d_2, \alpha)$ is calculated as a function of just three variables, where d_1 and d_2 are the two O_c-O bond distances, while α is the $O-O_c-O$ bond angle and O_c the central atom. The experimental values for d_1 , d_2 , α , and the dissociation energy are $2.4052a_0$, $2.4052a_0$, 116.75° , and 26.105 kcal/mol , respectively⁶⁵.

Figure 1 illustrates the PES of the $O_3(\tilde{X})$ molecule in a symmetrical vibration state, where the value of α is fixed at 116.8° and the $d_1 = d_2$. The compressed $O_3(\tilde{X})$ molecule is dominated by Coulomb repulsion and the results of all trial wave functions investigated here rather similar. However, whenever the $O_3(\tilde{X})$ molecule is stretched, static electron correlation becomes more important and the JAGP wave function superior due to the strong multi-reference character of the stretched $O-O$ bond. The dissociation energies at the experimental equilibrium geometry, using the JDFT-VMC, JDFT-LRDMC, JAGP-VMC, as well as JAGP-LRDMC methods are $-16.60(5)$, $-19.74(4)$, $-25.25(6)$ and $-26.14(5) \text{ kcal/mol}$, respectively. In fact, even in at the variational level, the JAGP wave function outperforms accurate LRDMC calculations based on the JDFT trial wave function and recovers $\sim 97\%$ of the experimental dissociation energy, while at the JAGP-LRDMC level the result is correct up to 0.1% .

The PES of the $O_3(\tilde{X})$ molecule in an asymmetrical stretching state is shown in Figure 2, where the value of α is again fixed at 116.8° . Defining δd as deviation

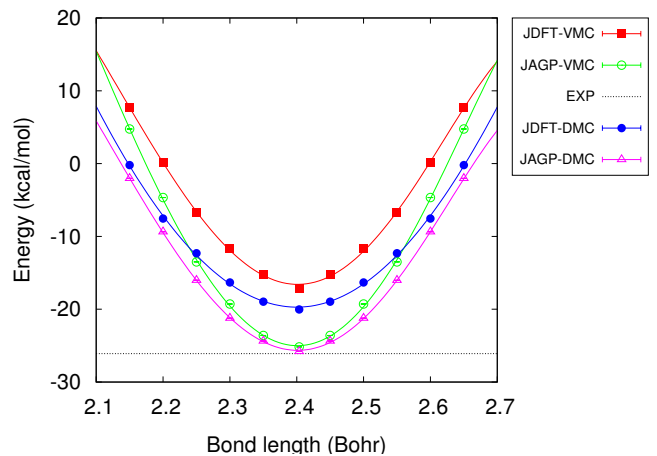


FIG. 2. (colour online) The PES of the $O_3(\tilde{X})$ molecule in an asymmetrical vibration state as obtained by the JDFT-VMC, JAGP-VMC, JDFT-LRDMC and JAGP-LRDMC methods. The energy normalization is such that zero energy corresponds to the ground state energy of $O_2(^3\Sigma_g^-) + O(^3P)$. The experimental dissociation energy is illustrated by the dotted line.

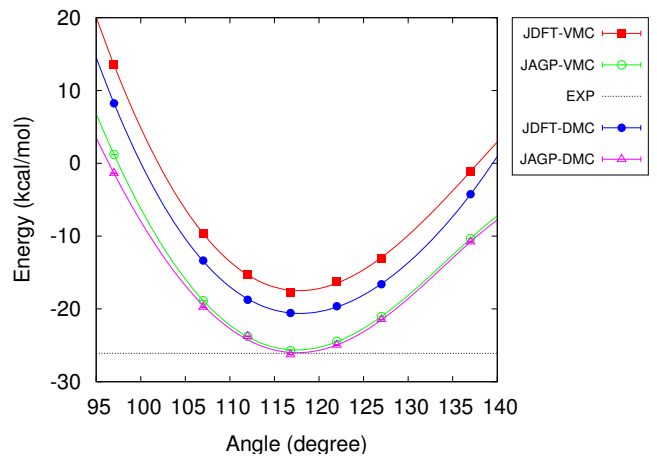


FIG. 3. (colour online) The PES of the $O_3(\tilde{X})$ molecule in a scissoring vibration state as obtained by the JDFT-VMC, JDFT-LRDMC, JAGP-VMC and JAGP-LRDMC methods. The energy normalization is such that zero energy corresponds to the ground state energy of $O_2(^3\Sigma_g^-) + O(^3P)$. The experimental dissociation energy is illustrated by the dotted line.

from the equilibrium bond length, each point on the PES corresponds to $d_1 \pm \delta d$ and $d_2 \mp \delta d$. Given the symmetry, $E(d_1 + \delta d, d_2 - \delta d, \alpha) = E(d_1 - \delta d, d_2 + \delta d, \alpha)$, as can be seen in the axial symmetry around the equilibrium bond length in Figure 2. The corresponding dissociation energies for the JDFT-VMC, JDFT-LRDMC, JAGP-VMC, as well as JAGP-LRDMC techniques are $-16.58(6)$, $-19.71(5)$, $-24.99(7)$ and $-25.64(5) \text{ kcal/mol}$, respectively. Interestingly, at equilibrium the JAGP is significantly superior to the JDFT trial wave function regardless of the particular QMC method, whereas for large asymmetries the LRDMC technique is essential.

Figure 3 exhibits the PES of the $O_3(\tilde{X})$ molecule in a scissoring state, where d_1 and d_2 are both fixed at $2.4052a_0$ and, thus, α the only variable. At the equilibrium bond angle, the dissociation energies as obtained by the JDFT-VMC, JDFT-LRDMC, JAGP-VMC and JAGP-LRDMC methods are -17.42(7), -20.55(5), -25.61(6), and -25.97(5) kcal/mol, respectively. Again, the JAGP systematically improves the description of the JDFT wave function. In fact, even at the JAGP-VMC method exceeds JDFT-based LRDMC calculations. Moreover, the small difference between the JAGP-VMC and JAGP-LRDMC schemes clearly demonstrates accuracy of the JAGP approach.

V. CONCLUSIONS

In summary, we find that the JAGP systematically improves upon the conventional JDFT wave function in

all cases we have considered here. In particular, except for the most asymmetric configurations, the JAGP-VMC method was able to outperform even more accurate LRDMC calculations based on the JDFT trail wave function. Together with the fact that the differences between the JAGP-VMC and JAGP-LRDMC results were rather small, this is a clear manifestation of the superiority of the JAGP wave function. In any case, the significant deviation between the JDFT and JAGP trail wave functions highlights that for a multi-reference system, such as the $O_3(\tilde{X})$ molecule, an accurate treatment of static electron correlation effects is essential.

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